Speciation and Characterization of Heavy Metal-Contaminated Soils Using Computer-Controlled Scanning Electron Microscopy

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In the analysis of heavy metal-contaminated soils, particle-by-particle determination of elemental composition (i.e. species or mineral) as well as the characterization of particle size, external and internal morphology, can be used to assess bioavailability, remediation potential and source. The imaging capabilities of the scanning electron microscope (SEM) coupled with the elemental analysis provided by energy dispersive spectroscopy (EDS) can be used to acquire both chemical and physical information. Heavy metal particles can be analyzed automatically using computer-controlled scanning electron microscopy (CCSEM). The analysis first recognizes a particle and determines is periphery and various size measures. An EDS spectrum is obtained, the constituent elements identified and the occurrence classified into a compositional type. A TIFF microimage with spectrum is saved for later off-line review and location coordinates are saved for on-line review.

Two examples illustrate the use of this technique in source identification. In one example, elevated levels of arsenic were attributed to a manufactured product rather than a fugitive source. In a second example, the lead-bearing constituents observed, as well as an association with a vuggy aluminosilicate occurrence and unburned coal, identifies coal ash as the probable source. © 2002 AEHS. Published by Elsevier Science Ltd. All rights reserved.

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Introduction

In general, regulatory agencies require soil and sediment to contain less than specified levels of heavy metals. To determine if soil metal contents are within regulatory guidelines, bulk samples are dissolved and subjected to an appropriate method of chemical quantitation or are ground to a powder and analyzed by X-ray fluorescence to yield heavy metal assays. These techniques can determine the concentrations very accurately, but information related to the chemical and physical (size, shape, internal particle structure) characteristics of the heavy metal occurrences and their carrier particles is lost in the process. The compositional and physical characteristics of heavy metal occurrences have been shown to influence bioavailability (see for example, Davis *et al.*, 1993, Gasser *et al.*, 1996, and Ruby *et al.*, 1999). The compositional characteristics of heavy metal contaminated soils have been recognized as a factor in remediation (see for example Ma *et al.*, 1995, Laperche *et al.*, 1996, and Eighmy *et al.*, 1997), and it seems that physical characteristics (size and enclosed/liberated nature of the occurrence) would affect the need for or the efficacy of remediation as well. Further, chemical and physical characteristics can be used to assist in the identification of contamination sources.

Determination of the compositional associations present is referred to as speciation. Speciation can be performed using powder X-ray diffraction, but this technique requires that the species of interest be present at a relatively high concentration, typically 5% or more. Historically, speciation has been attempted indirectly through sequential extraction or partial dissolution techniques. These methods involve selectively dissolving components using a sequence of increasingly rigorous reagents thought to be specific for certain minerals or mineral classes.

There are problems with this approach, including non-specificity of the reagents involved, creation of artifacts by the addition of partial dissolution reagents, and extraction schemes that are inappropriate for the mineral or mineral assemblages existing in the sample. Use of partial dissolution techniques may result in solublilization of the metal of interest that may then adsorb to other mineral surfaces not previously coated or containing significant adsorbed species. This tends to suggest that more metal exists in the adsorbed state than that actually occurs.

The speciation methods mentioned above provide no information on physical characteristics. In some cases, the heavy metal occurs as a single-component discrete particle, and in other cases, the heavy metal occurs within a complex particle of multiple components, some heavy metal-bearing and some not. The physical characteristics include the size and shape of the heavy metal occurrence and its carrier particle, and the association of the heavy metal component with other constituents if it occurs as a complex particle.

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The association can be described, for example, as liberated, enclosed, rim or cement.

The elemental association identification (speciation) as well as the physical description (size, shape, and association), can be performed on epoxy-impregnated polished mounts of soil samples by particle-by-particle analysis in the scanning electron microscope (SEM) or electron microprobe (EM) with their imaging capabilities and elemental analysis by energy or wavelength dispersive spectroscopy (EDS or WDS). When performed manually, potential heavy metal occurrences are identified by backscattered electron intensity (brightness) and composition determined by EDS or WDS (Davis *et al.*, 1993, Link *et al.*, 1994). The size (longest apparent axis) of heavy metal occurrences are estimated and the association described. Analysis generally continues for 5–8 h or until an established number of heavy metal occurrences have been described.

The recognition and characterization of particles can be performed by image analysis techniques. Krinsley *et al.* (1998) give an extended coverage of image analysis pertaining to SEM data. In the methods presented, images are acquired and then processed off-line to derive spatial attributes (size, shape, orientation, etc.). To derive compositional information, X-ray maps of multiple elements are acquired and stacked into a single multilayer image. X-ray maps require several minutes per field for acquisition.

A more efficient method of data acquisition is to process the "live" SEM image (see Henderson *et al.*, 1989), a procedure known as computer-controlled scanning electron microscopy (CCSEM). In this way, particles are recognized, measured, their elemental compositions and microimages acquired automatically. Before introduction of the Personal Computer (PC), these automated analyses were controlled by the microprocessor in the EDS detector. In the early 1980s, SEMs became more fully integrated with PCs (see for example Schamber, 1993) and CCSEM analysis became considerably more efficient. Some applications of CCSEM are illustrated in Schwoeble *et al.* (1988, 1990), Casuccio *et al.* (1983, 1989) and Song *et al.* (1999). The methods as applied to the analysis of heavy metals in soil is described herein and illustrated with two case studies.

Methods

Sample collection

Bulk soil or sediment samples are collected. As with any sample collection process, a strategy must be developed that both maintains the integrity of the sample and represents the area from which the sample is collected. Samples are collected using instruments such as plastic or Plexiglas that will not introduce contamination, especially metals, to the sample. In some cases the sample should be collected and maintained in a nitrogen atmosphere to limit the introduction of oxygen that may significantly alter speciation patterns. If human exposure is of interest, samples of residential soils close to the surface should be obtained in grassy areas, bare areas, near the drip-line of the residence, and in any areas where children play. Composite samples from deeper areas can be used to assess changes due to

differences in the soil geochemistry. Samples should be dried as soon as possible after collection to prevent continued chemical reactions.

Sample preparation

A "strewn mount" can be prepared quickly for SEM analysis by sprinkling disaggregated soil onto an SEM stub with double sided tape. Although preliminary information can be readily acquired, this preparation method does not allow internal particle structure (association) to be observed, and the EDS spectrum can be somewhat degraded by surface topography, making compositional characterization somewhat more difficult.

The preferred method of sample preparation is to produce an epoxy impregnated polished mount. Soil commonly displays a great range in particle size and should be sieved. The polished mount is usually either one inch or one and a quarter inches in diameter, and obviously, pebbles or larger particles need to be removed. This can be accomplished by sieving at 1000 µm (an arbitrary value) to remove very coarse sand and coarser particles. If the issue is one of ingestion, sieving may be performed to obtain a sample for analysis containing finer particles that are likely to adhere to surfaces that children place in their mouths. This size is not known with certainty, but 250 µm has been suggested (Que Hee *et al.*, 1985). Representative fractions of the whole sample and the various size splits should be saved for the determination of the heavy metal concentration in each size fraction using a suitable chemical technique.

To prepare the mount, a representative split of approximately one gram of the sieved dry sample is vacuum impregnated with epoxy in a ring and allowed to cure. A sample label is placed in the epoxy for permanent identification. The "puck" is polished to remove at the minimum a thickness of material equal to the radius of the largest particle. Polishing occurs using kerosene or isopar as a lubricant to avoid chemical reactions that might occur with water. This lubricant is removed with ethanol. Finally, the sample is given a thin coating of carbon to prevent charging while under the electron beam in a vacuum.

Sample analysis

The SEM analyses for the case studies presented here were performed on an RJ Lee Instruments (now Aspex Instruments) PSEM 75 using the ZepRun* software for CCSEM automation. Decisions related to the conduct of the automated analysis are established in a run parameter file, an element file and a rule file as described below.

Analysis set-up. The sample ring is scratched with two registration marks and small strips of carbon and copper tape are fixed to the upper surface before placing multiple samples into the SEM. The electron beam is saturated using an accelerating voltage of 20 KeV and imaging is set to the backscattered electron (BE) mode where the brightness of a component is proportional to its average atomic number (z). The image brightness and contrast controls are adjusted such that the

intensity of the carbon and copper tape are at established values thus assuring consistency in the analysis among all samples. In addition, a brightness threshold value is selected to separate components of potential interest (bright particles) from the background (less-bright particles and epoxy).

The epoxy and low atomic number occurrences such as coal appear as a dark background. The most common soil-forming components (e.g. quartz, feldspars, calcite, dolomite, clay) are intermediate in average atomic number and appear as a medium gray. Iron-bearing occurrences, not uncommon in soils, appear as a lighter gray, and heavy metal occurrences are bright. In complete characterization of all particles, the threshold value is chosen as just brighter than the particle substrate. This is referred to as an "all particle" run. A particle of potential interest in the context of heavy metal characterization is defined as one that is brighter than an appropriate intensity level chosen by the analyst. These bright particles are candidates for a heavy metal occurrence. This is referred to as a "high-Z" analysis. If heavy metals are concentrated (e.g. anglesite ($PbSO_4$) is 68% lead), the threshold level can be set quite high eliminating from consideration the vast majority of the particles. However, if heavy metals occur at low levels in a constituent (e.g. leaded iron oxide/hydroxide may have lead levels at a few percent), the threshold level must be set at a lower value resulting in more heavy metal-free occurrences being evaluated by EDS.

The area for analysis of each sample is defined by driving the stage to four edges of the circular puck and setting their X and Y coordinates and the focus. Establishing the focus at these known locations allows the focus to be calculated for any position on the sample in the event that the sample surface is not exactly horizontal. The stage is also driven to the two registration marks whose locations are also saved. The registration marks define a new (local or sample) coordinate system to replace the stage coordinate system. The first mark defines the origin and is assigned the X,Y coordinates of 0,0. The second mark defines the alignment or orientation of the X-axis which will pass through the identified point. Setting the origin and alignment to define a local coordinate system allows particles to be relocated even after the sample has been removed and replaced into the SEM days or years later.

Data acquisition. After the initial set-up, the SEM analysis begins under the control of the computer using instructions defined in the run parameter file. The stage is driven to the first field. The fields are selected either randomly if the whole surface is not to be analyzed (high magnification defined by the analyst), or selected to analyze all fields in order if the whole surface is to be analyzed (low magnification defined by the analyst). The field is inspected for pixels above the threshold brightness level to identify high-Z particles. Each particle of interest is sized and the electron beam is placed within that particle. The analyst can specify either the center of the particle, or rastered in the largest enclosed rectangle). The liberated X-rays are collected for a specified number of seconds using a light element detector and parsed into 2048 energy channels, each 10 ev wide. Each element produces

characteristic X-rays that are displayed as peaks at one or more specific energy levels. As the spectrum is being acquired, it is evaluated for elemental composition as determined by peaks in the EDS spectrum. The evaluation is only for elements selected by the analyst as indicated in the element file.

Due to the potential for overlapping peaks from different elements, the position and shape of the peaks are compared to spectra acquired on elemental standards to identify the elements and determine the number of X-ray counts attributed to each element. (See section *EDS Analysis and Peak Overlaps* for a discussion of issues related to overlapping peaks.) The EDS peak area for each element is expressed as a percent of the total area of all elements analyzed. In general, the EDS peak area percent increases and decreases as the element concentration increases or decreases, but it should not be considered as a weight percent. In the results presented herein, no corrections for atomic number, absorption, or fluorescence are made. Classification as minerals (known stoichiometry) is done by comparison to spectra collected from known standards. Changes in non-stoichiometric components can be expressed as changes in the EDS peak area as opposed to weight percent.

Although the light element detector processes information for fluorine to carbon, the sensitivity for these elements is less that that for the heavier elements. The lack of sensitivity makes the recognition and quantification of carbon and oxygen considerably less accurate. In addition, hydrogen is not recognized at all. These limitations make it difficult to separate oxides from carbonates, and impossible to distinguish oxides from hydroxides.

As the spectrum is being collected and the EDS area percents calculated for the high-Z particles, each occurrence is assigned to a class defined by the analyst in the rule file. At the minimum, this classification is used to separate particles of interest from particles that are not of interest. In the present context, a bright zircon ($ZrSiO_4$) particle would not be of interest, but a bright lead-bearing particle would be of interest. If the particle is of interest, the instructions can specify that the X-ray acquisition be extended (generally from 2 s to 5–7 s), and that a tagged information file format (TIFF) data object be saved. This data object contains the image at a specified pixel resolution (minimum 64 × 64 pixels, maximum 2048 × 2048 pixels), the 2048 channel EDS spectrum, and additional information related to instrument working conditions as well as particle physical measures and elemental composition. In addition to the data stored in tags, data consisting of the physical measures and the elemental composition and particle location are saved for all particles in table form for later review and summary.

The classification rules can be simple such as "heavy metal-bearing" and "other", or can be more complex in order to give a running total of the different components observed in the analysis. It should be noted that there is the opportunity to classify (and re-classify) particles after the analysis is complete so that the on-line classification may not be critical.

The analysis continues with the next particle in the field and additional fields are analyzed until a user-defined stopping criterion is met. The stopping criteria

include completing the defined area or reaching a predetermined number of fields, total number of particles, number of a specified particle type, or elapsed time. The stopping criteria used in these analyses was the entire 1 in. diameter mount for the low magnification analysis and 2 h for the higher magnification. Total analysis time was about 3 h. The analysis proceeds on the next sample in the specimen chamber until all samples have been analyzed. Four one-inch diameter samples can be placed in the standard sample chamber, but larger chambers are available.

Multiple magnifications. The fact that particles of interest in CCSEM analysis can occur in a wide variety of sizes presents the following problem — How much area should be analyzed? As a general rule, the smaller the particle, the more often particles of this type occur, but the less it contributes to the total volume or mass. After the analysis of a certain area, the number of occurrences for the smaller particles may be sufficient to statistically characterize their distributions, but the small number of occurrences of the larger particles may not be sufficient to characterize their distributions. Each doubling of the area (which would also double the analysis time) would provide additional information needed for the larger particles but would provide statistically redundant information for the smaller particles. To provide the needed information more efficiently, the analysis can be divided into two or three magnifications — a large area could be covered at a low magnification for the larger particles and a smaller area covered at a high magnification for the smaller particles. The area analyzed at each magnification is known and the data for the smaller particles can be prorated or normalized to the larger area.

In the case of multiple magnifications, there is a set of stopping criteria for each magnification. In the current context, the entire surface is inspected for particles larger than 5 or 10 μm, and 500–1000 randomly selected fields are inspected for particles down to 1 μm in diameter.

Data review. In the simpler studies, the CCSEM data may be totally satisfactory and not need much in the way of additional SEM review. When the particle morphology is complex, when the observed elements have severe peak overlap problems, or when it is important to understand the context in which the heavy metal occurrence is found, additional review may be required. At the completion of the analysis, the data can be reviewed on-line or off-line.

At the SEM, the stored image and spectrum can be reviewed, either by paging through all particles, or selecting only particles that have been assigned to certain heavy metal-bearing classes. Upon review of the stored data collected automatically, it may be desirable to reanalyze a particle to obtain a longer EDS acquisition, to assess the composition of associated components, or to obtain an image that puts the heavy metal component in the context of it's surrounding matrix. To accomplish this, pressing the space bar on the PSEM keyboard will move the stage to the location of that occurrence where the additional analysis can be performed. At the press of a button, a composite image can be saved to a file. The composite image consists of a

lower magnification view for context, a high magnification view illustrating the feature, and a labeled EDS spectrum. When in the review and relocation mode, a thumbnail image of the original image obtained by the CCSEM analysis along with the identifying particle number, classification and average size is superimposed on the composite image as well. The information saved in the TIFF image is illustrated in Figure 1.

In addition to the on-line review, all tabulated data and the images and spectra obtained in the CCSEM analysis can be reviewed using off-line programs. The data can be pre-sorted by class, element, size, etc. and the image and spectrum reviewed, either on a computer monitor, or as printouts consisting of multiple (2–30) image/spectrum pairs per page. In the analyses reported herein, manual review ranged from less than 1 h to about 2 h.

Remote review. In many cases, it is desirable to share the results of the analysis with other experts or clients who are not located at the SEM facility. The images and spectra are in a digital format and can be rapidly distributed over the Internet or on a CD for review with the appropriate software. However, questions may still arise that cannot be addressed adequately or quickly by photomicrographs. In this situation, manual review of the sample can be performed remotely using the WEBSEM®†, a fully functional remote control of the SEM over the Internet. The site with the PSEM functions as a host server and several remote viewers can observe the images and spectra as they are being collected. SEM control can be passed from the host to any of the remote sites. The remote function has the potential to significantly improve project coordination
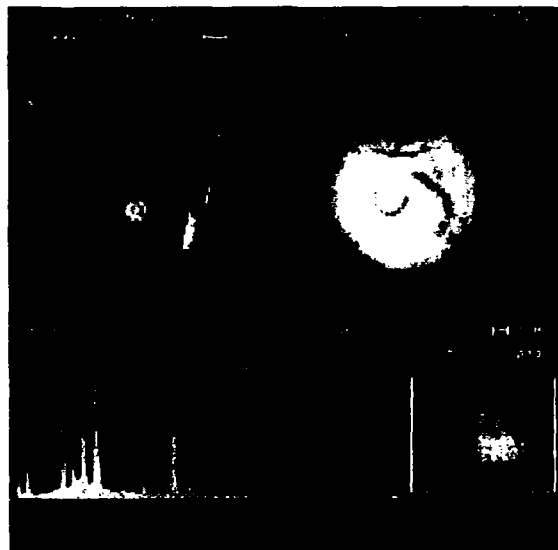

Figure 1 Composite SEM TIF image obtained during manual review of CCSEM-acquired data. The review program shows the EDS spectrum and microimage acquired during the CCSEM run in the bottom of the image, in this case for particle #X, with an average diameter of 5 16 μm and assigned to the Pb-Bearing class. This particle was relocated for additional manual review. The particle is shown to be spherical in the right image. The left image provides the context indicating that this particle was liberated. An extended EDS spectrum was acquired and replaces the automated spectrum

and reduce miscommunication, important factors especially in the initial stages when the nature and scope of a project are being defined, and in the later stages when the conclusions are being formulated.

Data summary. The particle-by-particle data generated by CCSEM can be summarized by classifying (reclassifying) the occurrences by elemental composition and tabulating various size distributions. Classes are defined by the user based on experience with known compositions and by compositional associations observed in the sample. In the present context, the

number percent and the area percent distributions by bins of average particle diameter are presented by compositional class. An example of the results of a two magnification run is given in Tables 1 3. Table 1 shows that 10 lead-bearing classes were defined and the remaining high-Z particles are assigned to "others". Approximately 19% of the high-Z particles were lead-bearing. After normalizing for the different areas analyzed at each magnification, the Number % as well as Area and Area % values are calculated. Tables 2 and 3 show the size distributions by number percent and area percent respectively. Instead of or in addition to average diameter, bins can be defined by other measures such as maximum diameter, aspect ratio or perimeter-to-area ratios.

Table 1. Example summary report for lead-bearing soils   summary distributions

Summary Distributions

Classes	#	Number (%)	Area (um²)	Area (%)
others	146	76.21	13463.6	87.20
PbPCa	18	13.60	1219.2	7.90
PbMnO	2	0.15	211.7	1.37
PbTi	5	3.64	133.9	0.87
PbP	2	1.78	116.1	0.75
Pb/S	2	0.15	97.9	0.63
Pb(Zn,Fe)	1	0.89	72.7	0.47
PbSi	1	0.89	45.4	0.29
Pb(AlSi)P	1	0.89	37.2	0.24
PbO	1	0.89	24.8	0.16
PbFeO	1	0.89	18.1	0.12
Totals	180	100.00	15440.7	100.00

Estimation of weight fraction

Bulk chemical analysis can obtain very accurate heavy metal assays that cannot be acquired on the SEM. The SEM obtains information regarding the proportions of the various components that cannot be acquired by bulk chemical analyses. A combination of the techniques can be used to estimate the amount of heavy metal contributed in each compositional class.

Knowing the relative volume of each heavy metal-bearing class, the density of each class, and the weight percent of the heavy metal in each class, the proportion of the total heavy metal contents in each class can be calculated. It has been shown that, for random sections of particulate that is itself in random orientation, the

Table 2. Example summary report for lead-bearing soils   size distribution by average diameter (microns)

Classes	Number (%)	Mean	Std Dev	1.0-2 5	2.5-5.0	5.0-10.0	10.0-20.0	20.0-50.0	> > >
Others	76.2	2.7	2.8	66.7	26.9	4.9	0.9	0.6	0.0
PbPCa	13.6	2.4	1.4	59.0	39 4	1.1	0.5	0.0	0.0
PbMnO	0.1	10.5	4.3	0.0	0.0	50.0	50.0	0.0	0.0
PbTi	3.6	1.7	0.7	98.0	0.0	20	0.0	0.0	0.0
PbP	1.8	2.2	1.0	50.0	50.0	0.0	0.0	0.0	0.0
Pb/S	0.1	7.4	0.1	0.0	0.0	100.0	0.0	0.0	0.0
Pb(Zn,Fe)	0.9	2.7	0.0	0.0	100.0	0.0	0.0	0.0	0.0
PbSi	0.9	2.1	0.0	100 0	0.0	0.0	0.0	0.0	0.0
Pb(AlSi)P	0.9	1.6	0.0	100.0	0.0	0.0	0.0	0.0	0.0
PbO	0.9	1.6	0.0	100.0	0.0	0.0	0.0	0.0	0.0
PbFeO	0.9	1.3	0.0	100.0	0.0	0.0	0.0	0.0	0.0
Totals	100.0	2.6	2.5	66.9	27.7	4.2	0.8	0.4	0.0

Table 3. Example summary report for lead-bearing soils   Area Distribution by average diameter (microns)

Classes	Number (%)	Mean	Std Dev	1.0-2 5	2 5 5 0	5 0 10 0	10 0 20 0	20.0-50 0	> > >
others	87 2	15.4	14.0	12.7	25 0	16 6	12.4	33.3	0 0
PbPCa	7 9	4 7	3 7	22 8	59 4	4 9	13 0	0.0	0 0
PbMnO	1 4	13 4	3.1	0.0	0 0	15 8	84.2	0.0	0.0
PbTi	0 9	2 7	1.9	75.9	0 0	24.1	0.0	0.0	0 0
PbP	0 8	2 9	0 7	14 4	85 6	0 0	0 0	0 0	0 0
Pb S	0.6	7.4	0.1	0.0	0 0	100 0	0 0	0 0	0 0
Pb(Zn,Fe)	0 5	2 7	0.0	0.0	100 0	0 0	0 0	0 0	0.0
PbSi	0 3	2 1	0.0	100 0	0 0	0 0	0 0	0 0	0 0
Pb(AlSi)P	0 2	1 6	0 0	100 0	0 0	0 0	0 0	0 0	0 0
PbO	0.2	1.6	0 0	100.0	0 0	0 0	0 0	0 0	0 0
PbFeO	0 1	1 3	0 0	100.0	0 0	0 0	0 0	0 0	0 0
Totals	100 0	14.1	13 6	14 5	27 6	15 9	13 0	29.0	0.0

area percent observed on the surface of a sample of particulate is equal to the volume percent in the sample as a whole (Chayes, 1956). Having determined the total assay, the amount of a heavy metal contributed from each compositional type can be estimated. For example, assume that a sample containing 813 mg/kg (mg/kg) As and 656 mg/kg Pb comprised three heavy metal classes in the relative proportions indicated by the volume percent column in Table 4. The weight fraction of the total mineral that is the heavy metal is shown in Wt. Fract. column. If the total volume of heavy metal-bearing occurrences was 100 cm^3, the total weight of the each class is the product of the volume and the specific gravity. The total weight of the heavy-metal in each class is the product of the component weight and the heavy metal weight fraction. The relative proportion of the heavy metal in each class can be applied to the total heavy metal assay to determine the contribution in mg/kg from each class. In this case, 661 mg/kg of the arsenic would be attributed to arsenolite (As_2O_3) and 162 mg/kg to lead arsenate ($Pb_3As_2O_8$). Similarly, 421 mg/kg of the lead would be attributed to lead arsenate and 235 to anglesite ($PbSO_4$).

EDS analysis and peak overlaps

X-rays of characteristic energy are generated by the jump of electrons to lower energy states after electron vacancies are produced by the interaction of beam electrons and specimen electrons. Higher atomic number atoms produce a more complex spectrum because these atoms have a more complex electronic configuration. The resulting peaks in the spectrum are named for the shell into which the electron jumps (e.g. K, L or M). Although the complete X-ray spectra of elements do not overlap with each other, it is possible for individual peaks generated by two or more elements to be closely spaced or even largely overlapping. Unfortunately, this is the case with some of the heavy metals. Lead has an M peak that has a severe overlap with the sulfur K (Figure 2(a)) and molybdenum L peaks. The same is true to a lesser extent with mercury, thallium and bismuth. Lead can be differentiated from sulfur by the presence of smaller peaks at 10.5 and 12.6 KeV for lead (Figure 2(b)). The major peak (L) for arsenic has a severe overlap with the magnesium K peak (Figure 2(c)) and a secondary

Table 4. Distribution of arsenic and lead in three compositional class in a sample with an arsenic concentration of 813 mg/kg and a lead concentration of 656 mg/kg

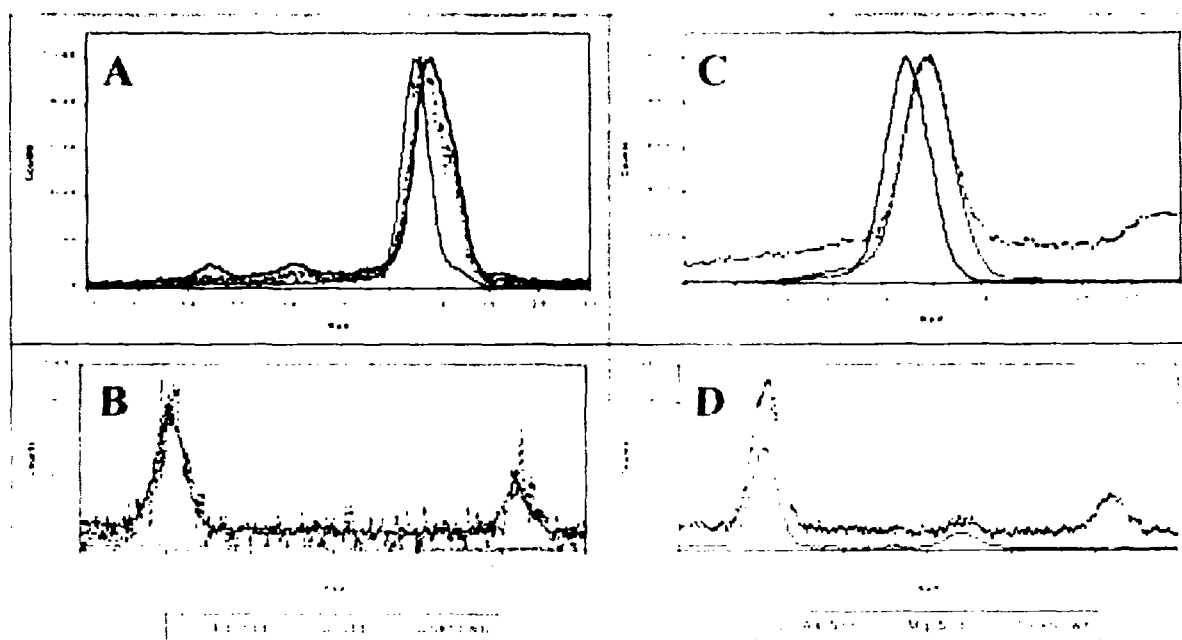| Class | Formula | (wt. fract.) | | Spec. Grav. | Vol (%) | (wt/100 cm^3) × 2 | | (ppm) × 2 | |
		As	Pb			As	Pb	As	Pb
Arsenolite	As_2O_3	0.757	0.000	3.865	50	146.4	0.0	651	0
Lead Arsenate	$Pb_3As_2O_8$	0.167	0.691	7.3	30	36.5	151.3	162	421
Anglesite	$PbSO_4$	0.000	0.683	6.2	20	0.0	84.7	0	235

Figure 2. EDS energy spectrum showing critical regions for potential overlaps of lead sulfur (a, b) and for As Mg (c, d). Figure 2b indicates that lead is present, but the slight offset to the left in Figure 2a indicates that sulfur is present as well. The exact overlap of peaks in Figure 2c indicates that magnesium is not present. In Figure 2d, the presence of arsenic is confirmed by the peak at 11.7 KeV. The presence of a peak at 12.6 KeV and the predominance of the 10.5 KeV peak over the 11.7 KeV peak indicates that lead is present as well

arsenic peak (K) overlaps with a lead L peak (Figure 2(d)). However, the overlapping peaks are not in exactly the same position nor are they identical in shape. When the heavy metal is present in moderately high concentrations (greater than about 10%) the peak curve fitting program in the automated analysis does a good job of unmixing the spectra. When the heavy metal is present at lower levels, a manual review and the collection of an extended count spectrum and more detailed curve comparison may be needed to confirm or deny its presence.

Case Studies

Two case studies are presented in which the source of heavy metals in contaminated residential soils are investigated. In each case, the offending heavy element is alleged to have originated from a nearby industrial site. In one case study, the soil on the property of the alleged source was sampled to serve as a reference which assisted in interpreting the results. Case study #1 illustrates CCSEM where the primary component of interest is an arsenic oxide. Its physical characteristics are relatively simple and manual review was not required to characterize the association. However, both lead and magnesium were present in the sample making automated identification of arsenic difficult when present in minor amounts. Manual review and extended EDS acquisition was performed on many particles. In case study #2, lead was the primary component of interest. It occurred in a complex association with other high-Z occurrences and required substantial manual review. In addition, manual SEM observations of components that were not actual carriers of the lead were required for the interpretation of source.

Case study #1: Arsenic in residential soils

Background. Residential soil samples within about one mile of an industrial metallurgical site were found to contain elevated arsenic concentrations. High levels of soil arsenic ranged from 500 to 1000 mg/kg with one occurrence of over 6000 mg/kg. Due to the proximity to an industry that was known to have arsenic by-product on its site, it was considered possible that the industry was the source of the residential arsenic distributed through the process of airborne dispersion.

If the elevated soil arsenic was due to contamination by airborne dispersion from the industrial site, then it would be expected that: (1) the spatial distribution of heavy metals and metalloids (arsenic in this case) would be consistent with that dispersion model; (2) the residential soils would be contaminated by the other heavy metals also observed in the industrial site and in similar ratios; (3) the specific arsenic occurrences would be consistent with those observed at the industrial site, and (4) no other significant source could be identified. Therefore, in addition to the arsenic analysis, the samples were analyzed for other elements including cadmium and lead.

Relative to the first two points, review of the spatial distribution patterns of the various elements, and the relative proportions of the various elements determined by bulk chemistry techniques indicated that the results

were not consistent with the suspected industry source. However, it could be argued that contamination could have occurred long enough ago that subsequent chemical reactions in the soils could adjust the relative proportions.

CCSEM analysis. A CCSEM analysis of the soil particulate to characterize the arsenic occurrences was undertaken on a total of 29 samples for the purpose of addressing points 3 and 4 above. Eleven of the samples were residential soils containing various amounts of arsenic (11–6754 mg/kg). Fifteen samples were derived from four location settings on the industrial site (IS) where arsenic content ranged from 100 to over 8000 mg/kg. Three samples were used as background samples (on site but less than 19 mg/kg in arsenic contents). The samples were sieved at 250 μm and prepared as polished pucks then analyzed at two magnifications for occurrences of heavy metals. Six samples were analyzed twice to assess reproducibility. Due to the EDS overlap of arsenic peaks with magnesium and lead, all potential arsenic occurrences were manually relocated and reviewed.

In addition to occurrences containing only arsenic and oxygen, arsenic was found associated with one or more elements. By far the majority of the occurrences were associated with calcium, antimony, aluminum, cadmium, and lead, but minor occurrences with silicon, iron and zinc were also observed. The total arsenic contribution from all occurrences of each compositional class was estimated for each sample. The density of each compositional type was assumed to be that of the closest stoichiometric mineral and arsenic content in each compositional type was estimated using a semiquant program. Those types contributing more than 5% to the total arsenic load are presented in Table 5. Images collected at 64 × 64 pixel resolution during the automated analysis representative of the combined groups are shown in Figure 3.

Results of IS and background samples. In the IS setting 1, 29% of the arsenic was associated with calcium, 21% was associated with Sb, 17% was associated with Cd, and 13% was associated with Pb. In the IS setting 2, 79% of the arsenic was associated with Pb with small amounts associated with Ca and Cd and none associated with Sb. In the IS setting 3, the most common arsenic association was with Ca (25%). Second in abundance was arsenic associated with aluminum (40%). About 16% was associated with Cd and 9% with Pb. In the IS setting 4, most of the arsenic

Table 5 Twenty percent attributed to arsenic-bearing classes in the suspected Industrial Source sites and the Residential Soils. (Only shows compositional classes totaling 5%, total As or more.)

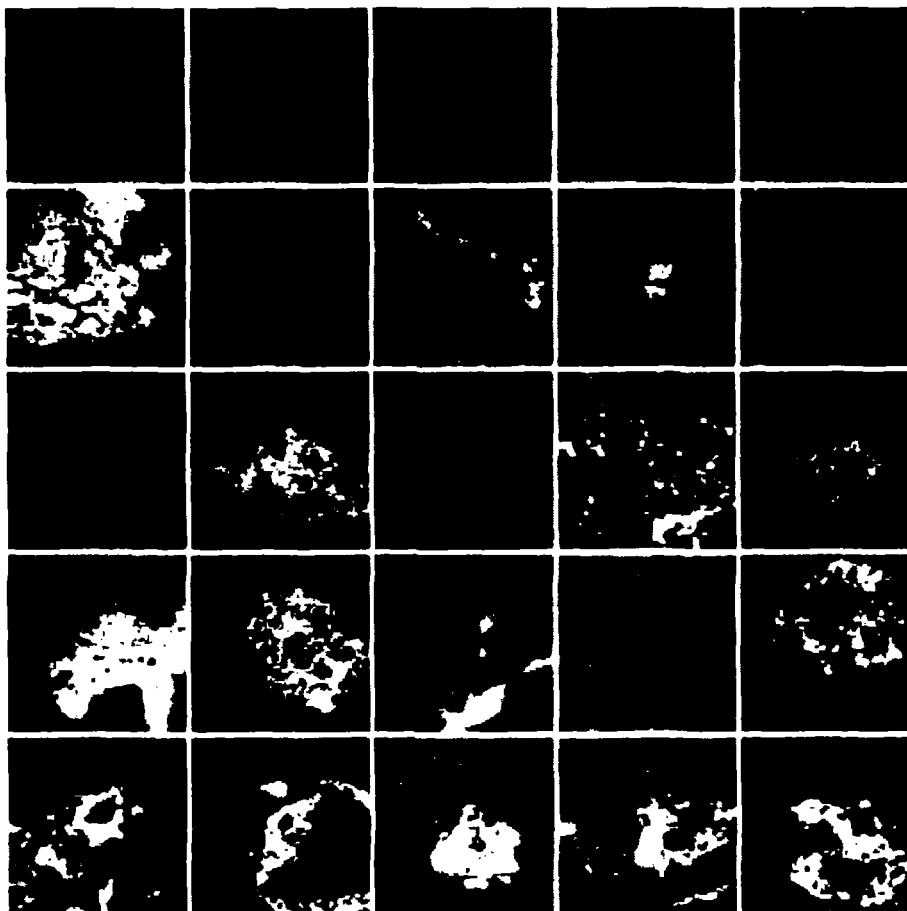| Phase	IS 1	IS 2	IS 3	IS 4	Soils
As Ca	29		25	..	
As Al			40	–	
As Sb	21				
As Cd	17		16		
As Pb	10	79	9	78	9
As O					84

Figure 3. Five examples each of arsenic associated with calcium (top row), antimony, aluminum, cadmium, and lead (bottom row). These low-resolution (64 × 64 pixels) images were acquired during the automated analysis. In all cases, the arsenic was associated with the brightest regions
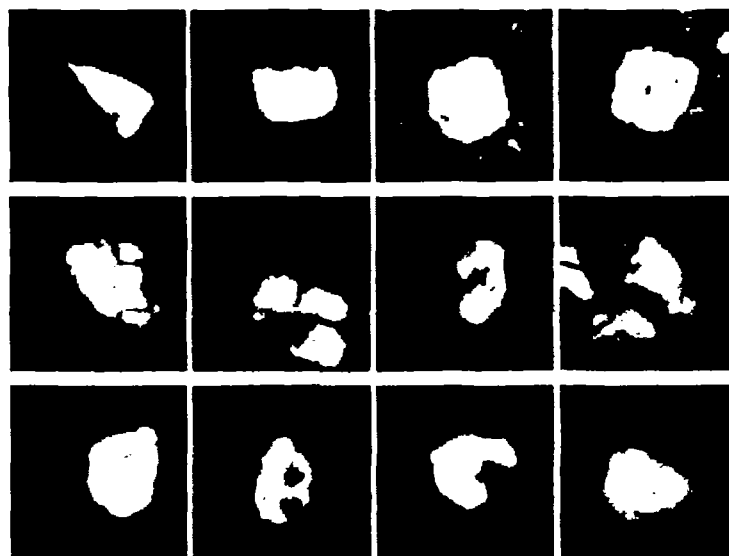

Figure 4. Four examples from three samples of the dominant arsenic oxide occurrences in the anomalous soils. These low-resolution (64 × 64 pixels) images were acquired during the automated analysis.

was associated with lead (78%), whereas most of the remaining arsenic occurred as very low concentrations. Very low levels of arsenic were observed in the background soils, but most of that was associated with lead.

Results of residential soils. In the anomalous soils, over 84% of the arsenic occurred as a quite pure arsenic oxide, but occasionally containing a trace of Cd. Most of the remaining arsenic (9%) was associated with Pb. In addition, review of the images indicate that the occurrences are generally solid discrete particles (Figure 4), in contrast to the majority of occurrences in the other settings where it occurred more often closely associated with other constituents in compound particles (compare the images in Figures 3 and 4). In addition, the size distribution of the arsenic particles was rather limited. Over 70% of the particles were between 10 and 20 μm in average diameter and 93% were less than 30 μm.

Conclusions. The spatial distribution of arsenic and other heavy metals as well as the ratios of the various heavy metals is not consistent with the hypothesis that the industrial site was the source of the arsenic in residential soils. The specific arsenic-bearing occurrences in samples derived from the site are not consistent with this hypothesis either. The majority of the arsenic in residential soils occurs as particles of arsenic oxide with small amounts of cadmium. The particles occur in a narrow size range and chemical purity of the occurrences of arsenic in the residential soils suggest that they were derived from a manufactured rather than a fugitive source. One candidate is a product that has been used for crabgrass control. It is a combination of arsenic trioxide (25%) and lead arsenate (8.25%). The proportion of arsenic from the arsenic trioxide is 82.4%. This is in the same general proportion as that observed in the anomalous soils. It is concluded that it was the use (or misuse) of a product like this that resulted in the elevated arsenic content of the residential soils in question.
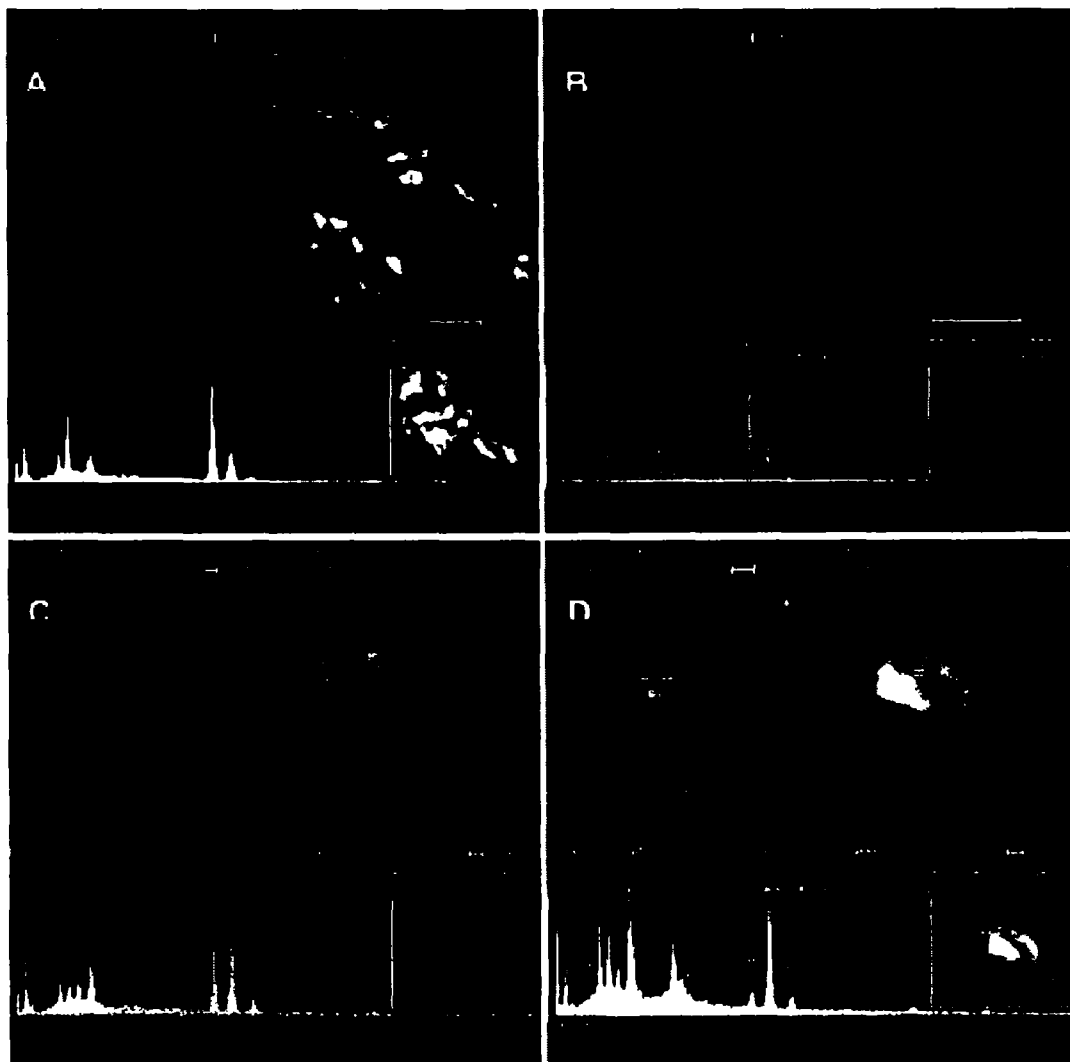

Figure 5 Review images and spectra of leaded manganese (a and b) and leaded iron (c and d) occurrences.

Case study #2: lead in residential soils

Background. Soils in the front, side and back yards of residential properties in the vicinity of an industrial operation involving lead sulfate were found to contain elevated levels of lead (up to 2000 mg/kg). Due to the proximity of the residences to the primary truck route from the industrial site, it was considered possible that the lead was derived from that site and distributed to properties near roadways by truck traffic.

If the elevated lead were due to contamination by lead transported by trucks from the industrial site, then it would be expected that: (1) the spatial distribution of lead would be consistent with that transport mechanism, (2) the lead would occur as an original sulfate or display a re-precipitated morphology, and (3) no other source could be identified. The spatial distribution of lead on the residential properties was consistent with a traffic source in that the lead concentrations were higher in the front and side yards than the back yards.

The concentrations did not decrease with increasing distance from the site, however, as would be expected if the lead source was from the industrial site raising the question of whether the lead was derived from an alternate source.

SEM analysis. Eleven samples were prepared for SEM analysis for the purpose of addressing points 2 and 3 above. Samples were sieved at 1000 μm and prepared as polished pucks for high-Z CCSEM analysis related to the heavy metal content. Due to the morphological complexity of the heavy metal-bearing components, all occurrences were relocated and inspected manually. In addition, each sample was examined by manual SEM techniques to characterize other anthropogenic constituents in the soil.

Results of the high-Z analysis. The results of the high-Z analysis indicated that there were four lead-bearing compositional classes. The two dominant classes are a
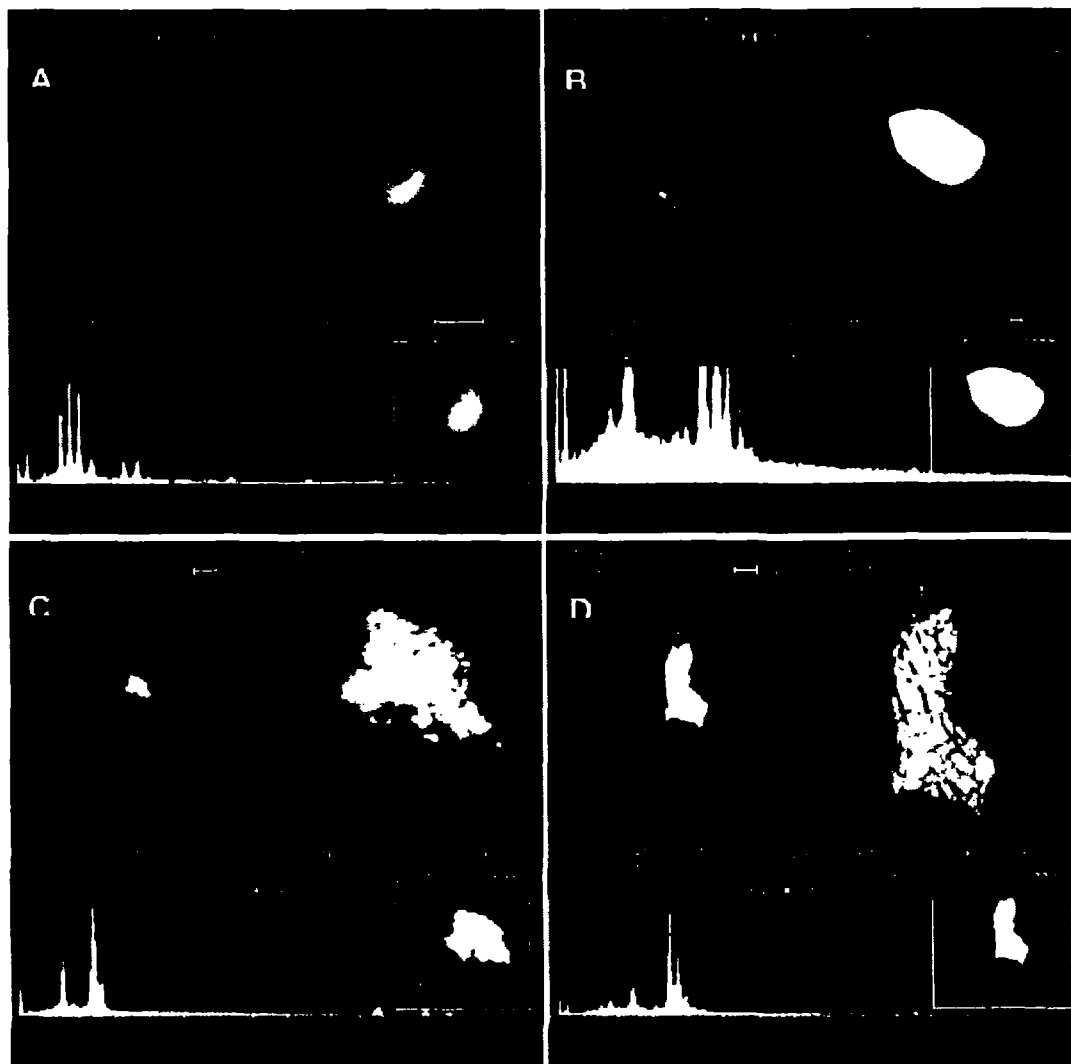

Figure 6. Review images and spectra of spherical leaded phosphorus (a), enclosed leaded barite (b), lead bromochloride (c), and liberated leaded tin (d).

leaded manganese and a leaded iron. Iron was often observed in the manganese occurrences, and manganese was often observed in the iron occurrences and these are thought to be end members of a continuous mixture.

Over 97% of the leaded manganese occurrences contained silicon and/or aluminum in proportions ranging from very small peaks, to the dominant peaks. Calcium and potassium were commonly observed as well. The rare occurrence contained a trace of titanium. Most of these occurrences were not single-component, discrete particles. Instead, they occurred as an apparent cement or an otherwise complex association. As a result of this morphology or mode of occurrence, it is generally not possible to say with confidence that the aluminum and silicon are a part of the leaded manganese or was derived from an adjacent component. However, the occurrences that were larger than the beam interaction volume showed aluminum and/or silicon and it is assumed that this is true for the smaller occurrences. Many of the leaded

iron occurrences showed similar aluminum and silicon peaks. However, copper, antimony, titanium, or zinc were occasionally present also. Representative images and spectra acquired during manual review of the leaded manganese and iron are shown in Figure 5.

The leaded phosphorus occurrences were commonly associated with silicon and/or aluminum as well. In addition, approximately one quarter of the leaded phosphorus occurrences were spherical. Iron, and to a lesser extent zinc, were found with the phosphorus as well (Figure 6(a)).

All samples contained a barium and sulfur (probable barite - $PbSO_4$) component and 8 of the 11 samples contained a leaded variety of barite (Figure 6(b)). Rare occurrences included one lead bromochloride (Figure 6(c)), one leaded glass, one probable paint and two leaded tin (Figure 6(d)), presumably solder.

Other than a single occurrence, lead sulfate was not observed. The one occurrence was a 5 μm inclusion in a titanium particle that contained spherical holes.
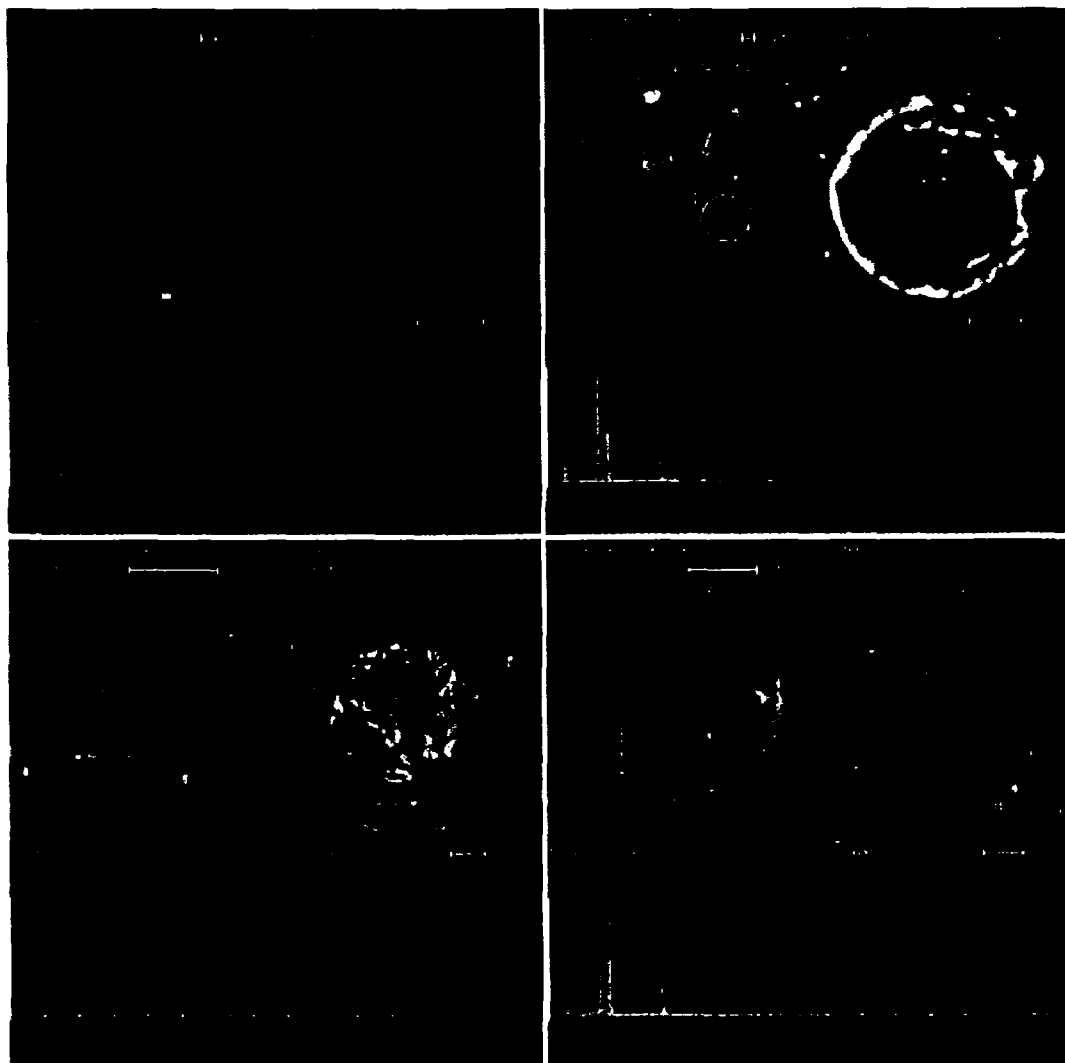

Figure 7   Images and spectra illustrating composition and morphology of the phase interpreted as bottom ash

Results of the manual SEM analysis.   Manual analysis of the samples revealed two unusual components in addition to the normal soil constituents of quartz, feldspars, calcium and magnesium carbonates, and clay. A component containing a major peak of silicon and aluminum at half to equal the silicon content, with traces of potassium, titanium, iron and, less commonly, calcium was also observed. These particles commonly contained vesicles and the particles themselves were occasionally spherical. This particle type is interpreted to be bottom ash resulting from coal combustion. Representative occurrences are shown in Figure 7.

A second unusual occurrence was carbon-rich containing a trace of sulfur and was interpreted as coal (Figure 8(a)). Rims or internal layers of a lead-bearing composition were common (Figure 8(b)). The coal commonly had inclusions, stringers or rims of the alumino-silicate composition, some of which having spherical vesicles (Figure 8(c) and (d)). The close asso-

ciation of the coal and the aluminosilicate component suggests that these are remnants of coal that were heated but remained unburned.

Discussion and conclusions.   The occurrence of ash and partially burned coal suggests an alternate potential source of lead other than the industrial site. The composition of representative coals and coal combustion products is reported in DOE (1996). These coals commonly have lead concentrations on the order of 10 mg/kg. This lead is not generally volatilized upon combustion of the coal and would be concentrated in the ash. Manganese and barium may be found in coal in higher concentrations (measured in 10s of mg/kg). Phosphorus may be found on the order of 0.1% and sulfur and iron greater than 1%. The oxides of silicon and aluminum may total in the range of 10%. The combustion of coal, then, could supply all the elements found associated with lead (leaded manganese and iron,
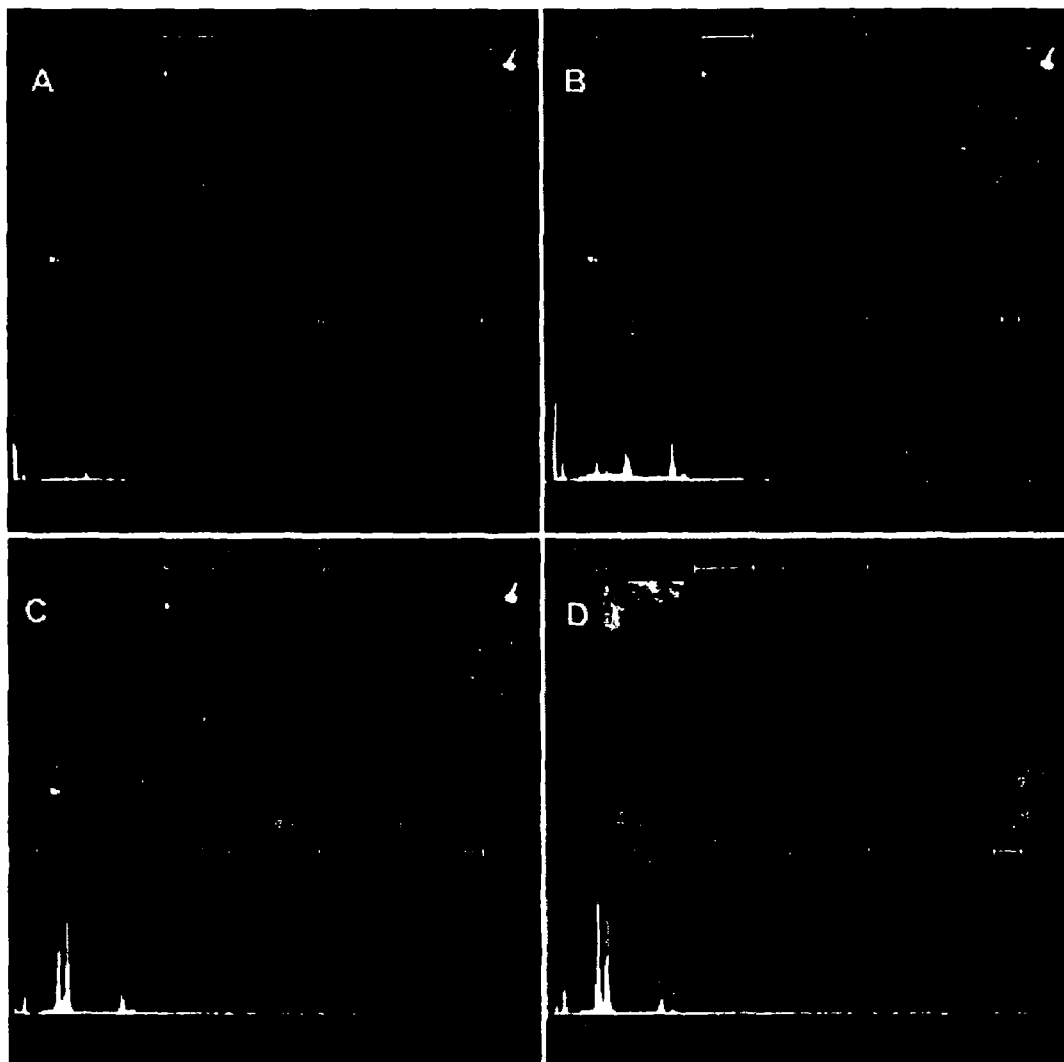

Figure 8. Images and spectra illustrating the composition of coal particle (a) with a lead-bearing rim (b) and associated aluminosilicate phase (c). The aluminosilicate phase also occurs enclosed in coal (d).

leaded phosphorus and leaded barite). In addition this process would also provide a source for the spherical nature of the leaded phosphorus.

Small amounts of bromomethane and chloromethane can be released from the combustion of some coals and this may be the origin of the lead bromochloride occurrence. The only occurrence of a lead sulfur component was observed as an enclosed particle in an ash fragment.

If the lead is derived from the coal burning process, a mechanism is also needed to transport the lead to the residential soil. The residential properties in this study are old and were historically heated by coal. It is known that some communities would collect the coal ash to use as traction material in the winter, and that some individual home owners would spread the ash on sidewalks and driveways for traction or on gardens and lawns as a fertilizer or conditioner. We suggest this as the origin for the majority of the lead in the residential soil of this study. We note that some of the lead in the samples was not described by CCSEM; the low levels in coal were not sufficiently bright to be detected, and had to be found in manual review. The association with the other non-leaded components was the key to understanding this origin.

Discussion and Conclusions

The description of heavy metal-bearing species, size, and association was shown to be critical in the determination or confirmation of source of the heavy metal contamination in the two settings illustrated. This information is only available using e-beam instruments — the scanning electron microscope or electron microprobe. The manual analysis of polished samples is time consuming, especially considering that concentrations may occur at levels down to several tens of mg/kg. However, automated analysis considerably reduces analysis time, even if considerable manual review is required, and should be considered as an ancillary tool in the analysis of heavy metal-contaminated soils and sediment.

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